Atmospheric oxygenation and volcanism Gaillard et al. reply

Fabrice Gaillard, Bruno Scaillet, Nicholas Arndt

Gaillard *et al.* reply

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REPLYING TO J. F. Kasting, D. C. Catling & K. Zahnle *Nature* 487**,**

Kasting *et al.*[1] question the model of ref. 2, in which we suggest that the oxygenation of the atmosphere, around 2.45 Gyr ago, was promoted by the emergence of subaerial volcanism, producing volcanic gases with much more elevated SO_2/H_2S ratios than submarine volcanism.

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Kasting *et al.*[1] claim that the enhanced SO_2/H_2S ratio in subaerial volcanic gases was accompanied by enhanced H_2 production, which may limit the oxidative capacity of emitted gases. This is only partly correct, because enhanced SO_2 also derives from the reaction[2, 3]:

$$S^{2-}(\text{melt}) + 3Fe_2O_3\,(\text{melt}) \rightarrow SO_2 + 6FeO\,(\text{melt}) + O^{2-}\,(\text{melt})$$

which implies that subaerial degassing extracts more oxygen from the melt than submarine degassing. The oxygen reservoir of the melt, a fundamental aspect of our model[3] that has so far not been taken into account, implies that more oxygen was therefore degassed as subaerial volcanism became abundant at about 2.7 Gyr ago.

Also, Kasting *et al.*[1] argue that the amount of outgassed CO_2 decreases by a factor of 3 as venting pressure decreases from 100 bar to 1 bar, which should limit production of organic carbon (CH_2O) and thereby limit the associated consumption[4] of atmospheric H_2. However, although the molar fraction of CO_2 in the gas decreases, the flux of CO_2 into the atmosphere is unchanged between 100 and 1 bar venting pressures[2], owing to the exceedingly low solubility of CO_2 in silicate melt in this pressure range (unlike the case for sulphur).

The *f* parameter of Holland[4] is used by Kasting *et al.*[1] to evaluate how much H_2 is consumed to reduce volcanic CO_2 into organic matter and SO_2 to pyrite. According to Kasting *et al.*[1], as pressure decreases, the *f* values of our calculated gas compositions indeed decrease (that is, their reducing power decreases, as required), but do not reach low enough values to drive the atmosphere to oxidizing conditions. However, the calculation of *f* is based on the way H_2S is produced or consumed in volcanic gases: Holland[4] first considered decomposition of H_2S during cooling, which is equivalent to production of H_2 (hence the $+3m(H_2S)$ term in the *f*

equation). The more recent analysis[5] by Holland considers instead that H_2S is the product of reaction between SO_2 and H_2 during cooling, a H_2-consuming reaction ($-3m(H_2S)$ in the *f* equation).

Conventionally, about 20% of volcanic CO_2 is consumed to produce organic matter[4]. Any variation of the amount severely affects the results of calculations made using the *f* equation, highlighting the difficulties in using it as to determine the oxidative capacity of volcanic gases. Holland's more recent analysis[5] of the causes of oxygenation suggests that oxidation was due to an increase in CO_2 and SO_2 volcanic fluxes, which is what our model predicts as volcanism changed from quasi-exclusively-submarine to partially subaerial. At this point, we stress that our model[2] not only describes an increase in the oxidative capacity of volcanic gas but also a chain reaction likely to facilitate atmospheric oxygenation. Of prime importance are the sulphate reduction processes, which should have been exacerbated by elevated volcanic SO_2 emissions. Biological sulphate reduction transforms sedimentary organic carbon into CO_2, which results in oxygen production[6]. In parallel, hydrothermal sulphate reduction, which decreases the reducing potential of hydrothermal fluids and fixes hydrothermal ferrous iron as pyrite, also contributed to atmospheric oxygenation[4]. All these reaction paths are not included in Holland's *f* factor, whereas they were certainly involved in the Great Oxidation Event.

We agree with the final recommendation of Kasting *et al.*[1] that both volcanic gases and hydrothermal fluids should be considered in models of the Great Oxidation Event. However, whereas we accept that thick Archaean oceanic crust was on average more mafic than younger crust, the uppermost layers—those most susceptible to hydrothermal alteration—would have consisted of olivine-poor basalt. In both modern oceanic plateaus and presumably in Archaean oceanic crust, parental picritic magma differentiates, leaving olivine cumulates at the Moho and erupting relatively evolved lava[7]. Basalt with little to no olivine is the dominant component of the upper parts of both modern oceanic plateaus and Archaean greenstone belts[7, 8]. These rocks are not susceptible to serpentinization; therefore little H_2 would have been produced during their hydrothermal alteration, and its impact on the atmospheric oxygenation should not have been as important as claimed by Kasting *et al.*[1].

Last, Kasting *et al.*[1] expressed concern about low-temperature re-equilibration processes between volcanic gases and basalts that were not considered by us[2]. We answer that this comment seems to re-introduce confusion between volcanic gas inputs (from mantle to exosphere) and hydrothermal recycling (seawater that reacts with basalts) that may arise

from a misinterpretation of ref. 9. Volcanic degassing and hydrothermal emissions are two fundamentally distinct processes, which not only differ in temperature, but chiefly differ in their source (igneous input versus surficial recyling).

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